cis,trans-Cyclohepta-1,3-diene as a Transient Intermediate in the Photocyclization of *cis,cis*-Cyclohepta-1,3-diene

Yoshihisa Inoue,* Shoji Hagiwara, Yoshihiko Daino, and Tadao Hakushi

Department of Applied Chemistry, Himeji Institute of Technology, 2167 Shosha, Himeji, Hyogo 671-22, Japan

The photocyclization of *cis,cis*-cyclohepta-1,3-diene (**1**) to give bicyclo[3.2.0]hept-6-ene (**2**) proceeds through a two-step process, in which the *cis,cis*-isomer (**1**) isomerizes photochemically to the highly strained *cis,trans*-cycloheptadiene (**5**) which in turn cyclizes thermally to give the bicycloheptene (**2**); the *cis,trans*-isomer (**5**) was trapped chemically by acidic methanol at room temperature to give the methanol adducts (**3**) and (**4**), and was detected spectroscopically upon low-temperature irradiation.

---

cis,cis-Cyclohepta-1,3-diene is known to cyclize to give bicyclo[3.2.0]hept-6-ene (**2**) in good yield upon irradiation,[1] in contrast to the preferred *cis–trans*-photoisomerization of the next higher homologue *cis,cis*-cyclo-octa-1,3-diene.[2] This process is believed to proceed through a photochemical disrotatory ring-closure following the Woodward–Hoffmann rule,[3] although the intervention of the *cis,trans*-isomer has been suggested.[4] In some reactions, *cis,trans*-cyclohepta-1,3-diene and its derivatives have also been postulated as transient species without any direct evidence,[5—7] while attempts to trap *cis,trans*-cyclohepta-3,5-dienone by using cyclopentadiene and furan were unsuccessful.[7c]

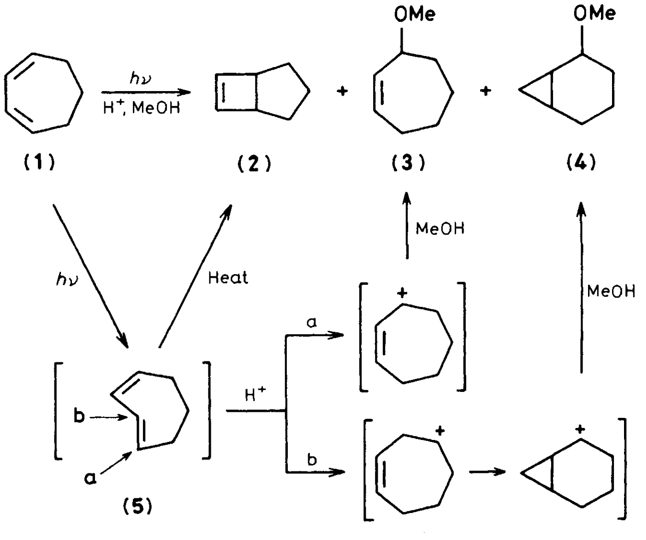
Our recent investigations have shown that the direct and the sensitized photolysis of *cis*-cycloheptene both produce the highly strained *trans*-isomer, which is stable at −78 °C and can be trapped by acidic methanol to give a methanol adduct.[8] This result and the reported photochemistry of cyclo-octa-1,3-diene[2] prompted us to study whether *cis,trans*-cyclohepta-1,3-diene was an unstable intermediate in the photochemistry of the *cis,cis*-isomer. We now present evidence for the presence of *cis,trans*-cyclohepta-1,3-diene in its ground electronic state, and report its chemical and spectroscopic properties.

Table 1. Direct photolyses of *cis,cis*-cyclohepta-1,3-diene (**1**).[a]

Solvent	$[H_2SO_4]$/M	Conv. (%)	Yield (%)[b] (**2**)	(**3**)	(**4**)
Pentane	0	68	96	[c]	[c]
Methanol	0	40	85	[c]	[c]
,,	0.03	46	75	1.5	1.5
,,	0.2	48	71	7.8	4.4
,,	1.0	36	32	27	13

[a] Irradiated at 254 nm for 20 min at room temperature under nitrogen. [b] Chemical yield based on cycloheptadiene consumed. [c] Not detected.

Direct irradiation at 254 nm of a 10 mM pentane solution of *cis,cis*-cyclohepta-1,3-diene (**1**) at room temperature gave



Scheme 1

bicyclo[3.2.0]hept-6-ene (**2**) in excellent yield† as reported earlier.[1] Photolysis in neutral methanol led to the same result, whereas irradiation in methanol containing 0.03—1.0 M sulphuric acid afforded additional products, *i.e.* 3-methoxycycloheptene (**3**) and 7-methoxybicyclo[4.1.0]heptane (**4**).‡¶ As shown in Table 1, the combined product yield§ of (**3**) and (**4**) increased with increasing acid concentration at the expense of the cyclization product (**2**). This result indicates the intervention of a common precursor to the products (**2**)—(**4**).

In order to identify this precursor, compound (**1**) was irradiated at 254 nm in an isopentane–methylcyclohexane matrix at −196 °C in a transparent quartz Dewar vessel. Figure 1 shows that the original absorption at 245 nm due to (**1**) decreased gradually, with an accompanying increase at 275 nm, an isosbestic point being observed at 270 nm (traces a—e). When the sample after 40 s irradiation (trace e) was kept in the dark for 30 min at −196 °C, no further change was observed. Warming of this sample to room temperature followed by recooling to −196 °C did not lead to recovery in the optical density at 245 nm, but the optical density decreased over the whole wavelength range giving trace f. Subtracting trace f from e gave the difference spectrum (e−f), which has a maximum at 272 nm and is ascribable to the unstable species which disappears upon warming. These spectral changes indicate: (i) that upon irradiation the *cis,cis*-isomer (**1**) does not cyclize directly to (**2**) but is first transformed into an intermediate which possesses an absorption maximum at 272 nm; (ii) that the intermediate is stable at −196 °C [it is unstable at −78 °C (see later)]; (iii) that upon warming, the intermediate does not isomerize geometrically regenerating the starting material (**1**) but is transformed into the final product (**2**) which has no absorption above 220 nm. Irradiation of the same solution at −78 °C also gave a similar reduction in optical density at 245 nm and an increase at *ca.* 275 nm, but the spectrum of the resulting species, which is analogous in shape to trace c in Figure 1, showed that it was not stable at this temperature. A plot of optical density at 270 or 280 nm *vs.* time showed an exponential decay and the reaction followed first-order kinetics with a rate constant of $2.3 \times 10^{-3}\ s^{-1}$ or a lifetime of 7.1 min at −78 °C for the decay of the transient intermediate. These results all support the intervention of *cis,trans*-cyclohepta-1,3-diene (**5**) as a common intermediate which undergoes thermal conrotatory cyclization to give (**2**) under neutral conditions and/or suffers protonation to give methanol adducts (**3**) and (**4**) in acidic methanol. [The lifetime of ~7 min at −78°C is too long for an electronically excited state of (**1**) to be the precursor of (**2**), and rules out direct conversion of (**1**)* into (**2**).] The photochemistry of cycloheptadiene may be summarized as in Scheme 1.

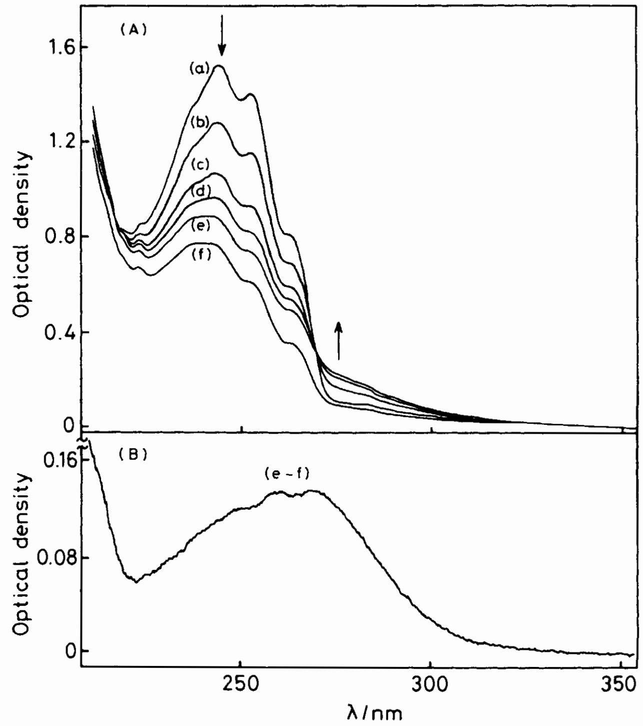


Figure 1. (A) Spectral changes upon direct irradiation at 254 nm of 0.12 mM *cis,cis*-cyclohepta-1,3-diene (**1**) in a 3:1 isopentane–methylcyclohexane matrix at −196 °C: (a) 0 s; (b) 10 s, (c) 20 s, (d) 30 s, (e) 40 s; (f) trace (e) warmed to room temperature and recooled to −196 °C. (B) Spectrum of *cis,trans*-cyclohepta-1,3,-diene (**5**) obtained by subtracting trace (f) from (e).

Assuming that the *cis,cis*-isomer (**1**) which is consumed upon irradiation at −196 °C is quantitatively transformed to the *cis,trans*-isomer (**5**), the molar extinction coefficient of (**5**) at −196 °C may be calculated, from analysis of Figure 1, as 2000 $dm^3\ mol^{-1}\ cm^{-1}$ at $\lambda_{max.}$ 272 nm, whereas the corresponding value for the *cis,cis*-isomer (**1**) is 10300 $dm^3\ mol^{-1}\ cm^{-1}$ at $\lambda_{max.}$ 245 nm. The bathochromic shift and the reduced molar extinction coefficient of (**5**) are characteristic of strained *trans*-cycloalkenes.[9—11]

Compound (**5**), containing a conjugated π system, possesses an unexpectedly short lifetime (τ 7.1 min at −78 °C) compared with 1-phenyl-*trans*-cycloheptene (4.2 min at ambient temperature),[9] *trans*-cyclohept-2-enone (>17 min at ambient temperature),[10] or *trans*-cycloheptene (45 s at 25 °C).[8] This may be attributed both to the feasibility of the unimolecular ring-closure process which is not accessible for the above-mentioned *trans*-cycloheptenes and also to the twisted *trans*-double bond of (**5**), which possesses a favourable conformation for the allowed conrotatory ring-closure and therefore accelerates the process as has been demonstrated in the ring-closure of *cis,trans*-cyclo-octa-1,3-diene at 80 °C.[2]

---

† All irradiations were carried out in quartz tubing or cell under nitrogen, using a 30 W mercury resonance lamp fitted with a Vycor filter. Gas chromatographic analysis was performed on a 1.5 m column of Apiezon L, which gave satisfactory separation of compounds (**1**)—(**4**) and cycloheptane internal standard. In order to avoid direct injection of highly acidic methanol and tailing of the solvent peak, the methanol solution was usually poured into aqueous sodium carbonate, the mixture extracted with pentane, and the pentane extract chromatographed, although direct injection of methanol solution gave no significant difference.

‡ A control run showed that, in the dark, a methanol solution containing 10 mM (**1**) and 1.0 M sulphuric acid did not give detectable consumption of (**1**) or formation of (**3**) or (**4**) after 3 h at room temperature, while the same mixture gave the adduct (**3**) in 5% yield after 21 days at room temperature or in 6% yield upon 20 h refluxing.

¶ The products (**3**) and (**4**) isolated from a large-scale irradiation by preparative g.c. showed identical i.r., n.m.r., and mass spectra and g.c. retention times with those of authentic specimens synthesized independently.

§ Relatively rapid and quantitative thermal conversion of (**4**) into (**3**) occurred at room temperature in the presence of higher concentrations of sulphuric acid. That the (**3**)/(**4**) ratio increases with increasing acid concentration, as shown in Table 1, does not indicate the intervention of different precursors to (**3**) and (**4**), but rather may be accounted for in terms of the above mentioned acid-catalysed conversion of (**4**) into (**3**).

This work was supported in part by grants from the Saneyoshi Scholarship Foundation, the Shorai Foundation for the Promotion of Science and Technology, and the Ministry of Education of Japan, which are gratefully acknowledged.

Received, 10th June 1985; Com. 793

References

1 W. G. Dauben and R. L. Cargil, *Tetrahedron*, 1961, **12**, 186; O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, 1962, **84**, 1220.

2 W. J. Nebe and G. J. Fonken, *J. Am. Chem. Soc.*, 1969, **91**, 1249; Y. Inoue, Y. Daino, S. Hagiwara, H. Nakamura, and T. Hakushi, *J. Chem. Soc., Chem. Commun.*, 1985, 804.

3 R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970, p. 38; W. M. Horspool, 'Aspects of Organic Photochemistry,' Academic, London, 1976, p. 100; D. O. Cowan and R. L. Drisko, 'Elements of Organic Photochemistry,' Plenum, New York, 1976, p. 408.

4 N. J. Turro, *Org. Photochem.*, 1969, **2**, 28.

5 K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1968, 1235; L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Am. Chem. Soc.*, 1970, **92**, 7002.

6 W. Kirmse and H. Jendralla, *Chem. Ber.*, 1978, **111**, 1873.

7 (a) D. I. Schuster, B. R. Sckolnick, and F.-T. H. Lee, *J. Am. Chem. Soc.*, 1968, **90**, 1300; (b) L. A. Paquette, R. F. Eizember, and O. Cox, *ibid.*, 1968, **90**, 5153; (c) D. I. Schuster and D. J. Blythin, *J. Org. Chem.*, 1970, **35**, 3190; (d) D. I. Schuster and C. W. Kim, *J. Am. Chem. Soc.*, 1974, **96**, 7437; (e) D. I. Schuster and J. Eriksen, *J. Org. Chem.*, 1979, **44**, 4254; (f) N. Hoshi, H. Uda, K. Sato, and H. Hagiwara, *J. Chem. Soc., Perkin Trans. 1*, 1984, 769.

8 Y. Inoue, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1635; Y. Inoue, T. Ueoka, T. Kuroda, and T. Hakushi, *ibid.*, 1983, 983.

9 R. Bonneau, J. Joussot-Dubien, J. Yarwood, and J. Pereyre, *Tetrahedron Lett.*, 1977, 235.

10 R. Bonneau, P. F. de Violet, and J. Joussot-Dubien, *Nouv. J. Chim.*, 1977, **1**, 31.

11 M. B. Robin, 'Higher Excited States of Polyatomic Molecules,' Vol. 2, Academic Press, New York, 1975, p. 166; N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, 1964, **86**, 2811.